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R: 559

P. 04/18

Document 1

アロニックス®

Mシリーズ

アクリル系特殊モノマー・オリゴマー

東亜合成化学



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R.559

P.05/18

■アロニックスとは

アロニックスは、東亜合成化学が開発したアクリル系特殊モノマー・オリゴマーの商品名です。

現在市販されているアロニックスには、特殊アクリレート、ウレタンアクリレート及びポリエステルアクリレートがあります。

特殊アクリレート

低粘度であり、皮膚刺激性の低いものが多く、光硬化性が優れているなどの特徴を持っています。従って特殊アクリレートは、アクリル系オリゴマーの粘度を低下させたり、アクリル系オリゴマーの接着性、耐熱性、硬度及び硬化性を向上させるための反応性希釈剤として有効です。

ウレタンアクリレート

ウレタン結合を主鎖に持ち、強靱性に優れた塗膜が得られ、各種素材との接着性が優れるなどの特徴を持っています。

ポリエステルアクリレート

エステル結合を主鎖とし、アクリル系不飽和結合を分子内に1～数個持っており、他のアクリル系オリゴマーと比べて、比較的低粘度で液体のものが容易に得られ、他のポリマーやオリゴマーと相溶性が優れるなどの特徴を持っています。

アロニックスは、これらの特徴を生かすことにより、各種の硬化手段を用いることができます。

また、硬質から軟質タイプまで用途・機能に合わせ幅広い分子設計が可能です。

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R:559

P.06/18

アロニックス

■アロニックスの種類

アロニックスは、樹脂の構造、アクリロイル基の数により下表のように分類されます。

特殊アクリレートー

官能基数	アクリレート	特徴
単官能	M-101 フェノールEO変性(n=4)アクリレート	低粘度
	M-102 フェノールEO変性(n=4)アクリレート	
	M-111 ノニルフェノールEO変性(n=1)アクリレート	低毒性
	M-113 ノニルフェノールEO変性(n=2.5)アクリレート	
	M-117 ノニルフェノールEO変性(n=2.5)アクリレート	良柔軟性
	M-120 N-ビニル-2-ピロリドン	
2官能	M-210 ビスフェノールA EO変性(n=2)ジアクリレート	A-EPE4
	M-215 イソシアメロールEO変性ジアクリレート	
	M-220 トリアロビレングリコールジアクリレート	TPGDA
	M-233 ペンタエリスリトールジアクリレートモノスタアレート	
	M-240 テトラエチレングリコールジアクリレート(n=4) (PEG#200)	TEGDA
	M-245 ポリエチレングリコールジアクリレート(n=6) (PEG#400)	
	M-280 ポリエチレングリコールジアクリレート(n=14) (PEG#600)	PFGDA
	M-270 ポリアロビレングリコールジアクリレート(n=13)	
3官能	M-305 ペンタエリスリトールトリアクリレート	PETA
	M-309 トリメチロールプロパントリアクリレート	
	M-310 トリメチロールプロパンPO変性(n=1)トリアクリレート	TMPTA
	M-315 イソシアメロールEO変性トリアクリレート	
	M-320 トリメチロールプロパンPO変性(n=2)トリアクリレート	
	M-360 トリメチロールプロパンEO変性(n=1)トリアクリレート	
多官能	M-400 シベンタエリスリトールペンタ及びヘキサアクリレート	DPHA
	M-450 ペンタエリスリトールテトラアクリレート	

ーウレタンアクリレートー

官能基数	アクリレート	特徴
2官能	M-1100	真実型 中硬質タイプ
	M-1200	無真実型 中硬質タイプ
	M-1210	無真実型 低ヤング率
	M-1310	真実型 軟質タイプ
	M-1600	無真実型 速硬化・中硬質タイプ

特殊アクリレートー

官能基数	アクリレート	特徴
単官能	M-5000 シリーズ	-COOH, -OH 差 含有モノマー

ーポリエステルアクリレートー

官能基数	アクリレート	特徴
2官能	M-6000 シリーズ	低毒性、低粘度
	M-7000 シリーズ	低毒性、高光沢、高硬化性
多官能	M-8000 シリーズ	低毒性、高硬度、高硬化性
	M-9000 シリーズ	耐熱性、高硬度、高硬化性

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R:559

P. 07/18

製造番号 (No.)	分類	構造式	分子量 (Mn)	分子量 (Mw)	粘度 (cP)	特性	特性
M-305 (PETA)	特殊アクリレート (3官能)	$(CH_2=CHCOOCH_2)_3CCH_2OR$ ペンタエリスリトールトリアクリレート	300以下	400-800/25	1以下	4以下	1.181/25
M-309 (TETA)		$CH_2=CHCOOCH_2)_3CCH_2CH_3$ トリメチロールプロパントリアクリレート	200以下	80-140/25	1以下	0.5以下	1.111/25
M-310		$(CH_2=CHCO-(OC_6H_4)_2OCH_2)_3CCH_2CH_3$ トリメチロールプロパンPO変性(n=1)トリアクリレート	400以下	50-110/25	1以下	1以下	1.061/25
M-315 (PETA)		$CH_2=CHCOOCH_2)_3CCH_2CH_2COOCH=CH_2$ イソシアヌレート80変性トリアクリレート	500以下	600-1,200/50	1以下	1以下	1.388/21
M-320		$(CH_2=CHCO-(OC_6H_4)_2OCH_2)_3CCH_2CH_3$ トリメチロールプロパンPO変性(n=2)トリアクリレート	500以下	70-170/25	1以下	1以下	1.043/25
M-350		$(CH_2=CHCO-(OC_6H_4)_2OCH_2)_3CCH_2CH_3$ トリメチロールプロパンBO変性(n=2)トリアクリレート	300以下	50-70/25	1以下	1以下	1.109/25
M-360		$(CH_2=CHCO-(OC_6H_4)_2OCH_2)_3CCH_2CH_3$ トリメチロールプロパンBO変性(n=2)トリアクリレート	300以下	85-85/25	1以下	1以下	1.108/25
M-400 (PETA)	特殊アクリレート (5官能以上)	$(CH_2=CHCOOCH_2)_3C-O-C(=O)-R$ R: HXは-CO-CH=CH ₂ ジペンタエリスリトールペンタアクリレート	300以下	3,500-6,500/25	1以下	3以下	1.188/25
M-450 (PETA)	特殊アクリレート (4官能)	$(CH_2=CHCOOCH_2)_4C$ ペンタエリスリトールテトラアクリレート	200以下	60-100/50	1以下	1以下	1.185/50
M-1100	ウレタンアクリレート (2官能)	$CH_2=CHCOO-R'-OOCNH-$ -R'-NHCOO-(ポリオール)-OOCNH- -R'-NHCOO-R'-OOCCH=CH ₂	-	70,000-130,000/50	-	-	1.208/21
M-1200			-	120,000-220,000/50	-	-	1.208/21
M-1210			300以下	2,600-2,800/25	1以下	3以下	1.065/25
M-1310			80以下	80,000-180,000/50	-	-	-
M-1500			-	8,000-12,000/50	-	-	-

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R: 559

P. 08/18



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P. 09/18

Document 2

New Values Of the Solubility Parameters From Vapor Pressure Data

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The solubility parameters of a broad spectrum of solvents and chemicals are calculated from vapor pressure data using an expression derived from the relationship of Hildebrandt. In the case of high boiling liquids, the available vapor pressure data are found to be unreliable when extrapolated to room temperature and an alternate method of calculation is proposed. A structure correlation is made using the method of Small and new values of the molar cohesion constants are developed. The problem of associations of certain molecular species is discussed and the concept of chameleonic character introduced as a qualitative explanation.

INTRODUCTION

Although a few coatings chemists have long recognized the value of the contributions of Hildebrandt, Flory, Scott, Huggins, and others, in the areas of polymer solubility and compatibility—only in recent years have the developed theories been applied to solve practical problems encountered in the coatings industry. Perhaps the reason for the long span of time between theory and application—nearly 60 years since the initial work by van Laar—has been the inability of the theory to adequately predict the behavior of the complex mixtures required for practical vehicle formulations. However, as the coatings industry becomes more sophisticated, the principles set forth by those and other workers are being increasingly adopted.

The mathematical description of the solution process as first proposed by van Laar and later developed by Hildebrandt and Scatchard¹ is centered around a concept introduced, and termed the "solubility parameter," by Hildebrandt.

* Coatings Materials, South Charleston, W. Va.

The classic compilation of data by Burrell² in the middle of the last decade has served as a basis for extending the usefulness of the concept by more recent workers including Lieberman,³ Frausnitz,⁴ G. don,⁵ and Crowley *et al.*⁶ However, since the work Burrell there has been no concerted effort to refine and expand this basic information.

The initial purpose of this work is not to seek explanations for notorious exceptions to the theory but rather to re-examine the source of the data and reexpand it to a much broader working base.

DISCUSSION

Calculation of Solubility Parameter From Vapor Pressure Data

The solubility parameter is defined as:

$$\delta = \left(\frac{\Delta H}{V} \right)^{1/2}$$

where δ is the solubility parameter, ΔH the intermolecular energy, and V the molar volume. Since $\Delta E = \Delta H - P\Delta V$ the solubility parameter becomes:

$$\delta = \left(\frac{\Delta H - P\Delta V}{V} \right)^{1/2}$$

In the final analysis the calculation of the solubility parameter revolves around obtaining the value of the heat of vaporization. Burrell used an empirical equation developed by Hildebrandt for hydrocarbon and assumed the vapors behaved ideally. The parameter was calculated by Burrell and then corrected according to several empirical rules he developed.

It was decided to recalculate values for the solubility parameters from vapor pressure data and to extend the list as much as possible.

A search of the literature reveals that one of the

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R: 559

P. 10/18

NEW VALUES OF THE SOLUBILITY PARAMETERS FROM VAPOR PRESSURE DATA

More accurate expressions for calculating the heat of vaporization at a given temperature from available vapor pressure data is given by the Haggensmacher equations, (3) and (4):

$$P(V_L - V_G) = \frac{RT}{M} \sqrt{1 - \frac{P/P_c}{T/T_c}} \quad (3)$$

$$\Delta H = \frac{dp}{dT} \frac{RT^2}{M} \sqrt{1 - \frac{P/P_c}{T/T_c}} \quad (4)$$

where V_L = the specific volume of the gas phase
 V_G = molecular weight of the liquid phase
 R = gas constant
 T = temperature
 T_c = critical temperature
 P = pressure
 P_c = critical pressure
 ΔH = heat of vaporization

Using equations (3) and (4) and vapor pressure in the form of the Antoine equation (5):

$$\log P = \frac{-B}{t + C} + A \quad (5)$$

where P = pressure in mm Hg; t = temperature in °C; and A , B , C are constants. It is possible to derive an expression for the solubility parameter as shown in equation (6):

$$s = \left[\frac{RT}{M} \sqrt{1 - \frac{P/P_c}{T/T_c}} \frac{2.303 BT^2}{T^2 P_c (T + C - 273.15)^2 - 1} \right]^{1/2} \quad (6)$$

Consequently, the following data are necessary to calculate the solubility parameter of a pure liquid at any desired temperature: Antoine constants A , B , and C , critical temperature (T_c), critical pressure (P_c), density (ρ), temperature (T) in degrees abs., and molecular weight (M).

Generally it is desirable to obtain the value of the solubility parameter at 25 °C. In certain cases this temperature is beyond the range of the usual Antoine expression. An examination of the Antoine equation indicates the source of the error, illustrated by the somewhat exaggerated diagram shown in Figure 1. At pressures between P_1 and P_2 , the Antoine equation describes the vapor pressure-temperature relationship quite well. However, at lower and higher temperatures the deviation actually becomes intolerable and usually new sets of Antoine constants are obtained. Unfortunately, these new Antoine constants are not always available.

To circumvent this problem, an alternate means of reliably estimating the heat of vaporization at room temperature, from data at different (usually higher) values, is necessary. It has been found empirically that at pressures below atmospheric pressure the latent heat of vaporization follows the relationship:

$$\Delta H = \Delta H^{\circ} + \dots \quad (7)$$

In logarithmic form this becomes:

$$\log \Delta H = \frac{-m}{2.303} t + \log \Delta H^{\circ} \quad (8)$$

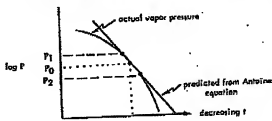


Figure 1—Illustration of fit of Antoine equation to experimental data (exaggerated for visual interpretation)

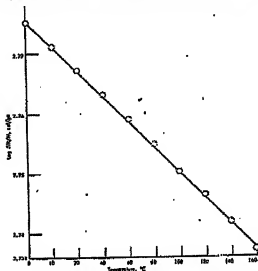


Figure 2—Effect of temperature on $\log (\Delta H/M)$ of water

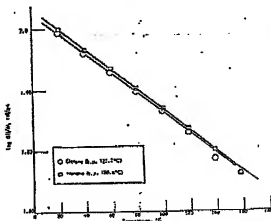


Figure 3—Effect of temperature on $\log (\Delta H/M)$ of normal hydrocarbons

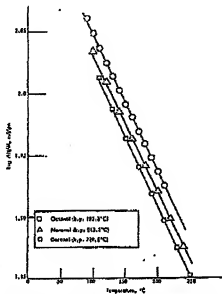
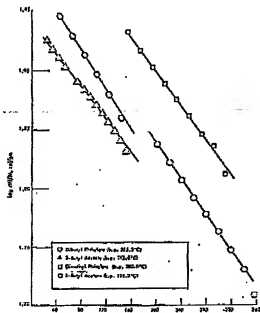
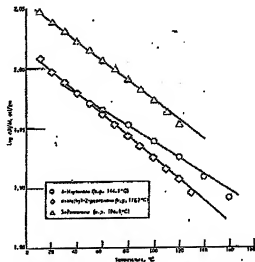
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R:559

P.11/18

K. L. HOY

Figure 4—Effect of temperature on log ($\Delta H/M$) of alcoholsFigure 5—Effect of temperature on log ($\Delta H/M$) of estersFigure 6—Effect of temperature on log ($\Delta H/M$) of ketones

where ΔH^* is the heat of vaporization at some standard temperature and m is a constant. A test of equation (8) is shown in Figures 2-6 for several different classes of compounds. As can be seen, the relationship seems to be quite general.

Using this relationship it is possible to estimate the heat of vaporization at 25°C by calculating the heat of vaporization in the temperature range in which the Antoine constants are valid and fitting these values into equation (8) to determine the slope (m), and (ΔH^*). With these two constants the heat of vaporization at 25°C can be estimated. Table 1 shows the results of such an extrapolation for a variety of compounds. Based on these results it is believed that the maximum error is above $\pm 4\%$ or translated to solubility parameter, approximately $\pm 2\%$.

The task of carrying out the calculations is relegated to a high speed digital computer. The data are tabulated in three forms: (1) an alphabetical listing, (2) a listing in order of increasing solubility parameters, and (3) in order of increasing boiling points. In addition to solubility parameters and boiling points, data on molecular weight, vapor pressure at 25°C and density in lbs./gallon at 25°C are included. Solubility parameter data for more than 680 compounds have been calculated and are shown in the tabulations. Some materials not normally considered solvents are included because of the usefulness of these data to chemists interested in finding reaction media for various processes. Moreover, it was desired to obtain as many different structural types as possible for a systematic correlation of structure and solubility parameter.

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R:559

P.12/18

NEW VALUES OF THE SOLUBILITY PARAMETERS FROM VAPOR PRESSURE DATA

Table 1—Comparison of Estimated and Observed Values of Solubility Parameters

solubility cal./cc.		H vap., cal./mole ¹	ΔG° , cal./cc. ^{1/2} /mole	δ^* cal./cc. ^{1/2}	Deviation in %
752	Valeric acid (Estimated)	16,305.40	1311.7	11,982	
192	(Observed)	16,907.41	1321.3	12,091	0.50
922	Methyl butanediol (Estimated)	16,602.88	1510.1	12,374	
327	(Observed)	16,989.57	1516.6	12,406	0.55
121	Decane (Estimated)	15,955.77	1512.5	7,848	
763	(Observed)	15,980.19	1512.5	7,719	1.67
361	Diethylbenzene (Estimated)	15,220.92	1352.2	8,515	
707	(Observed)	15,221.19	1354.8	8,718	1.38
931	Ethylstyrene (Estimated)	13,707.65	1347.3	9,015	
862	(Observed)	15,411.68	1345.9	9,520	1.05
229	Neomethylstyrene (Estimated)	15,181.76	1319.4	10,020	
025	(Observed)	15,540.33	1304.6	9,925	0.96
149	1,4-Dichlorobenzene (Estimated)	15,555.43	1293.7	10,005	
248	(Observed)	15,522.23	1291.1	9,991	0.72

(1) Form of Small's constants $\delta = \frac{H}{d} \cdot \frac{M}{V}$ (2) δ = solubility parameter.

Structure Correlations

Small² developed a method for estimating the value of the solubility parameter from chemical structure through additive group and constitutive molar attraction constants.

One of the objectives of the present project is to re-examine these molar attraction constants over a broad spectrum of compounds using multiple regression analysis. This is readily accomplished with high speed digital computers. In the course of this investigation it became apparent, as was expected, that the only compounds which did not reliably yield to analysis were the acids, alcohols and other compounds which are capable of association. The carboxylic acids, for example, were predictable only to the extent of $\pm 18\%$. It occurred to the author that since the simple analysis was based on monomeric acids, not the dimeric form, if the structural features of the dimers were

taken into account these compounds might fulfill the requirements for a successful analysis.

If it is assumed that carboxylic acids exist as dimers, then the following factors must be incorporated in the calculation of the solubility parameter. Equation (1) for solubility parameter can be expressed as:

$$\delta = \left(\frac{\Delta E_p}{M} \right)^{1/2} \quad (9)$$

where δ = solubility parameter (cal/cc)^{1/2}
 ΔE_p = molar internal energy (cal/mole)
 M = molecular weight (gm/mole)
 ρ = density (gm/cc)

Table 3—Correlation of Molar Volume Cohesion Of Glycol Ethers

Compound	Molar Volume Cohesion (cal/cc) ^{1/2} /mole (Observed)	(Calculated)	Error
Benzyl Cellulosate	1556.2	1577.7	1.4 %
Butyl Cellulosate	1501.4	1514.2	0.86 %
Cellulosate solvent	1043.7	1048.4	0.45 %
2-Ethylbutyl Cellulosate	1555.1	1543.9	0.72 %
2-Ethylhexyl Cellulosate	1735.0	1690.7	0.69 %
2-Nonyl Cellulosate	1638.2	1676.9	2.3 %
Methyl Cellulosate	1636.3	1580.0	0.96 %
cc-Methylbenzyl Cellulosate	1611.9	1674.5	3.8 %
Methyl Cellulosate	1606.3	1515.5	1.15 %
Nonyl Cellulosate	1622.9	1670.6	0.66 %
Butyl Cellulosate	1641.0	1646.7	0.35 %
Butyl Cellulosate	1676.5	1687.9	0.67 %
Carbitol solvent	1412.3	1422.1	0.69 %
2-Ethylbutyl Carbitol	1688.8	1671.6	1.5 %
2-Nonyl Carbitol	1756.1	1783.4	0.53 %
2-Ethylhexyl Carbitol	1996.5	1953.7	1.6 %
Phenyl Carbitol	1750.0	1698.0	2.3 %
Methyl Carbitol	1834.7	1818.4	0.88 %
Propyl Carbitol	1936.9	1954.1	1.17 %

Table 2—Correlation of Molar Volume Cohesion Of Carboxylic Acids

Compound	Molar Volume Cohesion (cal/cc) ^{1/2} /mole (Observed)	(Calculated)	Error
Acetic acid	1053.8	1014.3	3.9 %
Acrylic acid	1293.2	1268.1	1.9 %
Butyric acid	1566.3	1546.1	1.3 %
3-Ethoxypropionic acid	2040.9	2027.5	0.6 %
2-Ethylbutyric acid	2056.7	2055.5	2.4 %
2-Ethylhexanoic acid	2167.2	2137.1	2.0 %
2-Ethyl-3-propyl acrylic acid	2112.6	2155.5	0.9 %
Hexanoic acid	2022.6	2077.7	0.09 %
Isobutyric acid	1580.9	1473.9	6.7 %
Methacrylic acid	1581.1	1561.1	1.3 %
3-Methyl pentanoic acid	1872.9	2005.5	6.6 %
Propionic acid	1322.7	1280.3	3.2 %
Tetrahydrobenzoic acid	2082.0	2029.8	0.85 %
Valeric acid	1615.3	1511.9	19 %

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R: 559

P. 13/18

K. L. HOY

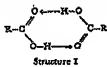
In the case of dimeric carboxylic acids, however, the actual molecular weight is two times the simple formula weight (M), and the solubility parameter becomes:

$$s = \left(\frac{18M}{M'} \right)^{1/2} \cdot \frac{\sqrt{F}}{2} \quad (10)$$

In a like manner the molar-volume cohesion (C) for dimeric carboxylic acids is given by equation (11):

$$C = \left(\frac{18M}{M'} \right)^{1/2} \cdot \sqrt{F} \quad (11)$$

The value of the solubility parameter of acetic acid when calculated from vapor pressure data and considered as an unassociated molecule is 13.01. However, when considered as a dimer, its value is 9.19. It is apparent that the dimeric form will have quite different solubility characteristics from the monomeric form, and it is therefore understandable that acetic acid is soluble in such diverse solvents as water ($s = 32.3$) as well as heptane ($s = 7.5$). Treatment of a series of 14 carboxylic acids by multiple regression analysis using the dimeric Structure I has given satisfactory results, as listed in Table 2.



Structure I

Another group of solvents which have evaded correlation by simple structure considerations are the glycol-ethers.* In these cases it is possible to postulate the



Structure II

intramolecular-hydrogen bonded Structure II. Using this structure it is possible to correlate the molar volume cohesion by regression analysis. The results of these correlations are shown in Table 3.

In this analysis, as well as in the case of the acid, over 640 organic compounds were considered. The samples consisted of aliphatic hydrocarbons, aromatic hydrocarbons, ketones, esters, and ethers. The overall analysis is the most reliable to date and accounted for 98.5% of the residual sum of squares. The molar attraction constants generated are given in Table 4.

Interestingly, a cursory examination of the solubility characteristics of the glycol-ethers reveals that certain members of these series, like the acids, are capable of being dissolved in polar solvents (water) and non-polar solvents (heptane). See Table 5 for effects of these and other structures. It would appear

* Cellulosic and Carbinol solvents, products of Union Carbide Corp.

Table 4—Molar Attraction Constants

Group	Molar Attraction (K) (cal cc ^{1/2} /mole)	Group	Molar Attraction (K) (cal cc ^{1/2} /mole)
-CH ₃	148.3	-S-	209.42
-CH ₂ -	151.5	Cl ₂	142.67
>CH-	85.99	Cl primary	203.06
-C-	32.03	Cl secondary	208.27
CH ₂ =	128.54	Cl aromatic	161.6
-CH=	121.65	Br	207.88
>C=	84.51	Br aromatic	205.50
-C≡ aromatic	117.12	F	41.53
-C≡	58.12		
-O- (ether, acetal)	114.88	Structure Feature	
-O- epoxide	176.50	Conjugation	23.26
-COC-	858.58	Cl ₂	-7.15
>C=O	202.56	7-ene	18.50
-CHO	222.64	4 Membered ring	17.76
(CO) ₂ O	547.25	5 Membered ring	20.29
-OH-	225.84	6 Membered ring	23.44
-H acidic dimer	50.47	Ortho substitution	9.69
OH aromatic	170.99	Meta substitution	6.6
NH ₂	255.58	Para substitution	40.52
-NH-	160.03	O	22.58
-N-	41.48	O-C	62.5
C≡N	354.49	Base Value	155.1
NCO	358.66		

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P. 14/18

Table 5—Effect of Structure on Solubility in Water and Hydrocarbon Solvent (Cont'd.)

Structure	Solubility in	
	H ₂ O	Heptane
$\begin{array}{c} \text{CH}_3-\text{CHCH}_3 \\ \quad \\ \text{C}_6\text{H}_5-\text{O} \quad \text{O} \\ \quad \\ \text{H} \end{array}$		
ethoxy-2-propanol	∞	∞
$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_3 \\ \quad \\ \text{CH}_2-\text{O} \quad \text{O} \\ \quad \\ \text{H} \end{array}$		
1-methoxy-2-propanol	∞	∞
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH} \\ \quad \\ \text{CH}_2-\text{O} \quad \text{O} \\ \quad \\ \text{H} \quad \text{OH} \end{array}$		
2-methyl 1,3 butanediol	∞	∞

that if the energy requirements can be fulfilled either by simple dimerization or intramolecular association, then that part of the molecule tends to adopt the character of the surrounding environment; i.e., in polar solvents the materials are capable of interacting as polar solvents, while in non-polar solvents the polar interactions are self-contained and the materials tend to behave in a non-polar manner. It is proposed that this ability to assume the character of the surrounding environment be termed "chameleonic" after the reptile which is able to assume the color of his background.

The chameleonic principle has wide ramifications when applied to practical problems; for example, the puzzling compatibility of the vinyl resin VAGH,* as compared to vinyl resin VYHH;† VYHH is a vinyl chloride-vinyl acetate copolymer and VAGH is a buck hydrolyzed version of VYHH. Yet VAGH has a broad

* Bakelite® vinyl resin, VAGH, product of Union Carbide Corp.
† Bakelite vinyl resin VYHH.



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spectrum of compatibility with polar and relatively non-polar solvents and resins in contrast to VYHH. Further inclusion of other hydroxy containing monomers in the polymer do not produce the dramatic effect of the vinyl alcohol moiety. However, if the vinyl chloride-vinyl alcohol unit operates as a chameleonic structure III then it would be expected that VAGH would have a unique broad spectrum compatibility and solubility which can not be duplicated by the use of other monomers such as hydroxy ethyl acrylate.



Structure III

This explains why certain glycol-ether** solvents are useful as coupling solvents for solubilizing relatively non-polar resins in water. The use of glycol-ethers†† to prevent blushing and cratering of non-polar resins during drying under humid conditions can also be explained by the chameleonic principle.

SUMMARY

Over 650 values of the solubility parameter have been calculated from vapor pressure data and presented in tabular form. From the data obtained it has been possible to expand the usefulness of Small's Molal Cohesion constants. The chameleonic nature of associated molecules is discussed as a means of understanding certain observed physical phenomena, particularly puzzling solubility characteristics of solvents which have evaded simple structure correlations.

ACKNOWLEDGMENT

The authors would like to acknowledge the invaluable work of Dr. R. A. Martin without whose service the mathematical analysis via computer would not have been possible. †

References

- (1) Hildebrand, J. H. and Scott, R. L., "The Solubility of Nonelectrolytes," 2nd ed. New York: Reinhold Publishing Corp., 1950.
- (2) Scatchard, G., *Chem. Rev.*, **5**, 231 (1951).
- (3) Burrell, H., *Official Digest*, **37**, No. 303, 706 (1955).
- (4) Lieberman, E. P., *Official Digest*, **34**, No. 444, 50 (1950).
- (5) Blanks, R. E. and Fraunholz, J. M., *Ind. Eng. Chem. Fundamentals*, **3**, (1964).
- (6) Gardon, J. L., *JOURNAL OF PAINT TECHNOLOGY*, **38**, No. 492, 43 (1966).
- (7) Crowley, J. D., Tague, Jr., G. S., and Lovett, Jr., J. W., *JOURNAL OF PAINT TECHNOLOGY*, **38**, No. 496, 209 (1966).
- (8) Hagenmacher, J. E., *J. Am. Chem. Soc.*, **68**, 1653 (1946).
- (9) Small, P. A., *J. Appl. Chem.*, **3**, 75 (1953).

** Selective Carbhidol, Cellosolve, and Propagol® solvents, products of Union Carbide Corp.
†† Cellosolve and Carbhidol solvents.

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Document 3

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ポリマーのSP値の予測—訂正と補足

井本 裕

先に本誌に接収剤のことを書き、ポリマーのSP値を予測する計算法のことを簡単に記した。そのさい不注意にも間違の名を書きちがえた。文献番号24b) Small, I. Appl. Polym. Sci. はJ. Appl. Chem. であった。そのこともあり、あらためてポリマーのSP値を予測するSmallとHovとRogersの報告をもうすこし詳しく書いておきたいと考える。

1. Smallの場合²⁾

1953年に出的報告で彼は溶液の熱力学から推しはじめる。きっちり詰められたページを超える論文は基礎的で時間をかけて勉強するに足る。しかし、ことはすべて省略し、SP値の予測の所だけに限る。Smallのその式は簡単に式(1)である。ポリマーのくり返し単位についてである。

$$SP = \frac{\sum F}{V} \quad (1)$$

Fというのは“molar-attraction constant”と彼が呼ぶもので、表1の値である。Vはモル容積($\text{cm}^3 \text{mol}^{-1}$)である。またFの単位は $(\text{cal cm}^3)^{1/2} \text{mol}^{-1}$ である。

表1 F(cal cm^3)^{1/2} mol⁻¹の数値(Small)

-CH ₃	214	-H	80-100
>CH ₂	133	-O-	70
>CH-	23	-CO-	275
>C<	89	-COO-	310 (エステル)
CH ₂ =	190	CN	410
-CH=	111	-Cl	270-260
>C=	19	-CCl ₂	260
CH ₂ C-	285	-CCl ₃	250
-C≡C-	222	-Br-	340
C ₆ H ₅ -	735	-I-	425
C ₆ H ₄ -(o,m,p)	658	-C ₆ H ₅	150
アクリル	1145	-C ₆ H ₄	274
5員環	105-115	-S-	225
6員環	98-105	-SH	315
共役系	20-30	-ONO ₂	440
		-NO ₂	440

計算例をあげた方が早分りする。

例(1) ポリスチレン



$$C_8H_8, M=104$$

$$d=1.05$$

$$\text{実測 SP}=8.0$$

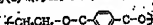
$$\sum F=133(\text{CH}_2)+28(\text{CH})+755(\text{C}_6\text{H}_5)=896$$

$$V=104/1.05=99$$

よって

$$\text{計算 SP}=896/99=9.05$$

例(2) ポリエチレンテレフタレート



$$C_{16}H_{14}O_4, M=192$$

$d=1.38$, 実測 $SP=10.7$, 1) に対する計算は下記のとくである。

$$\sum F=2 \times 133(\text{CH}_2)+2 \times 310(\text{COO})+658(\text{C}_6\text{H}_4)$$

$$=1534$$

$$V=192/1.38=139$$

よって計算 $SP=11.0$

Smallは $SP=10.7$ と計算しているが、それには $d=1.33$ としなければならぬ。

例(3) 二硝酸セルロース



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$$C_6H_8O_{10}, M=224, d=1.6, \text{実測 SP}=10.5$$

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R:559

P.16/18

[565] (52)

ポリマーのsp値の予測—訂正と補足

表2 Hoyの表の例(680種のうちから)

	分子員	沸 点 (760mm)	蒸気圧 (25℃, Mm)	SP*	比 重 (25℃, lb/Gal)**
ジエチレングリコール	106.12	245.7	0.00	14.24	9.288
トリメチル・ジメチルアミン	174.17	238.3	0.00	11.50	10.116
アセトニトリル	41.05	61.1	88.38	12.11	6.478
MMA	90.12	102.0	40.12	9.23	7.764

* 蒸気圧からの計算値, つまり実験値になる。

** 1ガロン=3.7853 dm³, 1 lb (重) = 0.4536 kg なので, 表にある数字に0.1198 をかけると, g/cm³の値になる。

計算は次のとおりである。

$$\Sigma F = 5 \times 28 (\text{CH}) + 133 (\text{CH}_2) + 3 \times 70 (-\text{O}-) + 90 (\text{H}) + 2 \times 440 (\text{ONO}_2) = 1453$$

$$V = 224/1.5 = 140$$

よって計算 SP = 10.4

以上, SP 値は計算で相当にうまく得られることが分る。なお実験 SP 値はすべて日本化学会誌「化学便覧」, 応用編」(丸善, 1973) p. 831 からとった。

2. Hoy の場合¹⁾

この42ページにわたる長い論文のうち36ページは表である。680種の化合物について, アルファベット順, SP 値順, 沸点 (°C) 順の3種に分けて表2のようなデータを掲げている。著者 Hoy はユニオン・カーバイド社の人(ウェスト・バージニアの Coating Materials 部)と出ているが, 大へんな努力の結果の表だろうと圧倒されたことであつた。

Hoy は Small の計算法を検討することから始めるのだが, 例えばメチル・セロソルブ(2)について。



$$\text{C}_3\text{H}_8\text{O}_2, M=76, d=0.9597, \text{よって } V=79.19$$

Hoy は蒸気圧から算出し SP = 11.58 (実験値) とした。

Small によって計算すると,

$$\Sigma F = 214 (\text{CH}_2) + 2 \times 133 (\text{CH}_2) + 2 \times 70 (-\text{O}-) + 90 (\text{H}) = 710$$

$$\therefore \text{SP} = \Sigma F / V = 8.97$$

全く一致しない。これは例えはメチル・セロソルブは上式でなく, 下式²⁾であろうとする。そういうことから



考えなおしたのであろう。Hoy は新しく表3を Molar Attraction Constant として呈出した。若干の計算例を出す。

例(1) メチル・セロソルブ

上出のように $V=79.19 \text{ cm}^3 \text{ mol}^{-1}$ である。

表3 Molar Attraction Constant

	[(cal/cm ³) ^{1/2} mol ⁻¹] (Hoy)		
-CH ₃	148.3	CS ₂	209.42
-CH ₂ -	141.5	CCl ₄	342.57
>CH-	85.99	CCl ₂ (一般)	205.06
>C<	32.03	CCl ₂ (二級)	208.27
CH ₂ =	126.54	CCl ₂ (芳香族)	161.0
-CH=	121.53	CBr	257.88
>C=	84.51	CBr (芳香族)	205.60
-CH= (芳香族)	117.12	CF ₄	41.33
-C= (芳香族)	98.12	(増分)	
-O- (エーテル)	114.98	炭酸系 ¹⁾	23.26
-O- (エポキシ)	176.20	炭酸系 ²⁾	7.18
-CO-O-	328.58	炭酸系 ³⁾	12.50 ¹⁾
>C=O	282.96	炭酸系 ⁴⁾	7.76
-CHO	292.64	炭酸系 ⁵⁾	20.98
-CO-	967.29	炭酸系 ⁶⁾	23.44 ¹⁾
-OH	225.84	炭酸系 ⁷⁾	9.69
-H (酸性イマー)	50.74	炭酸系 ⁸⁾	6.5
-OH (芳香族)	170.99	炭酸系 ⁹⁾	40.23 ¹⁾
NH ₂	225.56	炭酸系 ¹⁰⁾	22.56
-N-	61.08	炭酸系 ¹¹⁾	62.5
C≡N	354.56	炭酸系 ¹²⁾	
NCO	358.56	炭酸系 ¹³⁾	135.1

$$\Sigma F = 1483 (\text{CH}_2) + 2 \times 141.5 (\text{CH}_2)$$

$$+ 114.98 (-\text{O}-) + 225.84 (\text{OH})$$

$$+ 135.1 (\text{炭酸系}) = 907.22$$

よって $\text{SP} = \Sigma F / V = 11.46$ と計算される。

これで実験値 11.58 によく一致したと云いよう。

例(2) プタジエン・ジオキサイド(4)



$$\text{C}_4\text{H}_4\text{O}_2, M=86$$

SP, 実験値 11.78 (Hoy による)

$$d=1.1056, \text{よって } V=77.78$$

表3による計算。

$$\Sigma F = 2 \times 141.5 (\text{CH}_2) + 2 \times 85.99 (\text{CH})$$

$$+ 2 \times 176.2 (\text{エポキシ}) + 135.1 (\text{炭酸系})$$

$$= 942.48$$

よって $\text{SP} = 942.48 / 77.78 = 12.11$ (実験値¹⁾ 11.78)

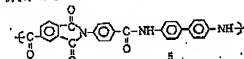
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P.17/18

例(3) ポリアミドイミド(5)



$C_{22}H_{17}N_3O_5$, $M=459.4$, $d=1.21$ とし表3で計算する。それは既に本誌に出ている。文献¹⁾の p.328 の表7である。それは Ghosh¹⁾ によるものであったが、

$$\begin{aligned} \Sigma F &= 15 (CH=O) + 9 (C=O \text{ 芳香族}) \\ &+ 4 (C=O) + 1 (-NH-) + 2 (NH) \\ &+ 1 (5 \text{ 員環}) + 1 (6 \text{ 員環}) + 1 (p \text{ 置換}) \\ &+ 1 (m \text{ 置換}) = 428.01 \end{aligned}$$

(環数なるとに換算があった。表の上から5行目の18103は18003, 8行目の4003は4033であった。そして: SP=1108と算出してあった。しかし Hoy の表3からみると Ghosh¹⁾ は基礎値の1351を加えるべきであった。即ち

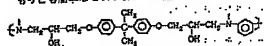
$$SP = (4208 + 1351) \times 121 / 459.4 = 1143$$

となる。半酸 (SP 1210) の際、N-メチル-2-ピロリドン (SP 1100) やジメチルホルムアミド (SP 1179) にいくらか溶けるのだから、今回の SP 1143 を採用したい。私は Ghosh のみを用いずして、原報によるべきであったと悔む。なお Ghosh は Hoy の表を用いて Small

の表と書いている。誤しも誤まるものだ、と思うと奇妙な気がする。

例(4) 簡単な硬化エポキシ樹脂

もっとも簡単なビスフェノール型エポキシ樹脂を m-



$C_{22}H_{27}O_5N_3$ ($M=449$)

フェニレンジアミンで硬化させたものはである。その ΣF は表3から容易にもとめられる。ただし、

$$\begin{aligned} \text{C}_6\text{H}_5 & \text{も } \text{C}_6\text{H}_4 & \text{も } 4 (CH=) + 2 (-C=) + p \\ & \text{または } m - \text{増分} \end{aligned}$$

で計算される。

$$\begin{aligned} \Sigma F &= (2 \times CH_2) + (4 \times CH_2) + (2 \times CH) + (2 \times C) \\ &+ (2 \times O-) + (2 \times OH) + (2 \times C_6H_5 - p) \\ &+ (C_6H_4 - m) + 2 (p - \text{増分}) + (m - \text{増分}) \\ &+ (2 \times N) + (\text{基置換}) = 408.83 \end{aligned}$$

よって硬化物の密度を1.2とすると

$$SP = 408.83 / (445 + 1.2) = 11.0$$

密度が1.3なら SP=11.9 である。

3. Fedors の場合¹⁾

Small の場合も Hoy の場合もうまくセットされている

表4 d_{E1} と d_{E2} (Fedors, 一部省略)

	d_{E1}	d_{E2}		d_{E1}	d_{E2}
CH ₃	1125	33.5	CONH ₂	10000	17.5
CH ₂	1180	16.1	CONH-	8000	8.5
CH	820	-1.0	CON<	7050	-7.7
C	350	-19.2	HCON<	6600	11.3
H ₂ C=	1030	28.5	HCONH	10500	27.0
CH=	1030	13.5	COCl	5000	38.0
C=	1030	-5.5	NH ₂	3000	19.2
HCE	920	27.4	NH	2000	4.5
C=	1690	8.5	N	1000	-8.0
φ	7140	71.4	-N=	2800	5.0
φ (o, m, p)	7530	52.4	CN	6100	24.0
φ<	7530	33.4	NO ₂ (硝基)	7000	24.0
φ<	7530	14.4	NO ₂ (芳香族)	3870	32.0
φ<	7530	4.6	NO ₂ (脂肪族)	2800	33.5
(φはフェニル基)			NCO	6900	35.0
>S 員環	250	16	-O-	800	3.8
s, s 員環	750	18	OH	7120	10.0
環の中の炭素二重結合			DH (ジ置換)	5220	13.0
1個ごとに	400	-2.2	-S-	3380	12
-O-CO-O-	4200	22.0	Cl (ジ置換)	2750	24.0
COOH	6600	28.5	Br	2300	26.0
CO	4300	18.0	I	3700	30.0
CO	4150	10.8	Al	4550	31.5
CHO	5100	22.3	Si	3300	22.0
-CO-O-CO-	7300	30.0		810	0

(* は略号、本文中のように算出した方がよい)

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R. 559

P. 18/18

[567] (54)

ポリマーのsp値の予測—訂正と補足

るが、ポリマーの密度 d が必要である。ここに新しい構造を紙の上で書いて、そのSP値を知ろうとするときの d が致命的なことになる。その点でこのFedorsの表4は役立つことになる。彼はモル容積の V をそれぞれの基のモル容積 d_{v_i} の和と考えるのである。

$$V = \sum d_{v_i} \quad (2)$$

そしてその d_{v_i} (25°C)を適当に表4のようにする。元来がSPは式(3)である。

$$SP = (CED)^{1/2} = \left(\frac{\Delta H - RT}{V} \right)^{1/2} \quad (3)$$

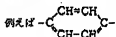
ΔH は融解熱である。この $(\Delta H - RT)$ も、

$$(\Delta H - RT) = \sum d_{e_i} \quad (4)$$

とする。そして

$$SP = \left(\sum \frac{d_{e_i}}{d_{v_i}} \right)^{1/2} \quad (5)$$

とする。表4から計算するのだが、*印のフェニル基だけは誤算で、実際は次のように計算した方がよい。



$$\sum d_{e_i} = 4 (\text{CH}=\text{C}) + 2 (\text{C}=\text{C}) + 3 (\text{共役二重結合})$$

+ 6 員環

$$= 4 \times 1030 + 2 \times 1030 + 3 \times 400 + 250 = 7630$$

$$\sum d_{v_i} = 4 \times (13.5) + 2 \times (-5.5) + 3 \times (-22) + 16$$

$$= 524$$

しかし表中の $d_{e_i} = 7630$, $d_{v_i} = 524$ とあっている。

例(1) 簡単なエポキシ樹脂

Hoyの場合の例(4)とした d について計算

$$\sum d_{e_i} = 2 \times 1000 (\text{N}) + 4 \times 1180 (\text{CH}_2) + 2$$

$$\times 820 (\text{CH}) + 2 \times 7120 (\text{OH}) + 3$$

$$\times 7630 (-\phi-) + 1 \times 350 (\text{C}) + 2$$

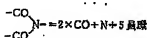
$$\times 1125 (\text{CH}_2) + 2 \times 800 (-\text{O}-) = 49690$$

$$\sum d_{v_i} = 277$$

$$SP = \left(\frac{49690}{277} \right)^{1/2} = (179.39)^{1/2} = 13.4$$

例(2) 上掲のポリアミドイミド(5)

d では問題になるのはイミド環だが、次のように考える。

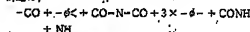


$$\sum d_{e_i} = 2 \times 4150 + 1000 + 250 = 9500$$

$$\sum d_{v_i} = 2 \times 108 - 9 + 16 = 215$$

として、あとは足し算すれば足りる。

構造は、



である。よって上の順に

$$\sum d_{e_i} = 4150 + 7630 + 9500 + 3 \times 7630 + 8000 + 2000$$

$$= 54170$$

$$\sum d_{v_i} = 108 + 33.4 + 28.6 + 3 \times 52.4 + 9.5 + 4.5$$

$$= 244$$

$$\left(\frac{\sum d_{e_i}}{\sum d_{v_i}} \right)^{1/2} = \left(\frac{54170}{244} \right)^{1/2} = (222)^{1/2} = 14.9$$

これは大にすぎると思われる。

4. 結 語

以上、前報の誤りを訂正し、加えて新しく全体を紹介した。簡単なエポキシ樹脂のSP値が似たと言っても誤解が高分子が溶解するとは思えないが興味がある。以上の3種の計算法で、どの方法が最良かは、見当が全くつかない。その高分子の密度 d が分ってあればHoyの方法が(d が分らねばFedorsの方法が)仕方がない)何だか計算しやすいように思う。なおSmallの方法は黄盛さんが1982年に紹介されている⁹⁾。なお私は別に T_g の予測法もまとめておいたが、こういう構造の高分子(または接ぎ物)はこれくらいのSPと T_g をもつだろう、と表上の計算をすることができれば良いだろう、と思う。

なお、他にもSP(や T_g)の予測法の報告があるだろうと想像する¹⁰⁾。御教示をたまわることができれば幸甚である。

文 献

- 1) 井本 雄, 日本技術協会誌, 22, 314 (1986).
- 2) P. A. Small, J. Appl. Chem., 3, 71 (1953).
- 3) K. L. Hoy, J. Paint Technology, 42, 76 (1970).
- 4) M. Ghosh, K. Maiti, J. Macromol. Sci.-Chem., A22, 1463 (1985).
- 5) R. T. Fedors, Polymer Engineering and Science, 14, 147 (1974).
- 6) 黄 盛盛, 「接ぎの化学と実用」, 第10刷(高分子学会, 1981), p. 24.
- 7) 井本 雄, 接ぎ, 30, 238 (1986).
- 8) 黄 盛盛, 「日本技術協会誌, 接ぎハンドブック」, 第2版(日刊工業新聞社, 1971), p. 110にD. W. Van Krevelen法というのが紹介されているが, SmallやHoyと類似のものらしいので省略した。



US00684381B2

(12) **United States Patent**
Suzuki et al.

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(45) **Date of Patent:** Jan. 18, 2005

(54) **AIR FILTER**

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(*) **Notice:** Subject to any disclaimer, the term of this
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§ 371 (c)(1),

(2), (4) **Date:** Jan. 23, 2002

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PCT Pub. Date: Nov. 29, 2002

(65) **Prior Publication Data**

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55/524; 55/528

(58) **Field of Search** 55/385.3, 486,
55/487, 524, 528, DIG. 5, DIG. 24, DIG. 28;
428/316.6, 534

(56)

References Cited**U.S. PATENT DOCUMENTS**

3,210,926 A * 10/1965 Harrington 60/202
3,922,437 A * 11/1975 Kitta et al. 428/383
4,976,858 A 12/1990 Kadoya
5,019,140 A * 5/1991 Bowser et al. 55/486
5,129,923 A * 7/1992 Hunter et al. 55/524
5,573,811 A * 11/1996 Townsley 55/524
6,336,947 B1 1/2002 Atsumi et al.
2003/0106293 A1 * 6/2003 Tanaka et al. 55/524
2003/0150199 A1 * 8/2003 Tanaka et al. 55/486

FOREIGN PATENT DOCUMENTS

JP 55-114323 * 9/1980 B01D/39/18
JP 63-14886 * 4/1988 B01D/39/18
JP 2-253815 10/1990
JP 6-343809 12/1994
JP 11-33319 2/1999
JP 11-300124 11/1999
JP 2000-70635 * 3/2000 B01D/46/12

* cited by examiner

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(74) *Attorney, Agent, or Firm*—Young & Thompson

(57)

ABSTRACT

There is provided an air filter, which has a long lifetime and permits to capture effectively carbon particles and reduce costs. The air filter has the first filter layer 11 impregnated with oil and the second filter layer 12, which is provided on the downstream side of the first filter layer 11 and serves as a lipophobic layer having an oil-repellent property. The filter material of the first filter layer 11 has a higher density than the filter material of the second filter material 12.

20 Claims, 9 Drawing Sheets

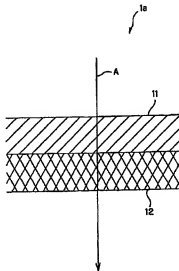


FIG. 1

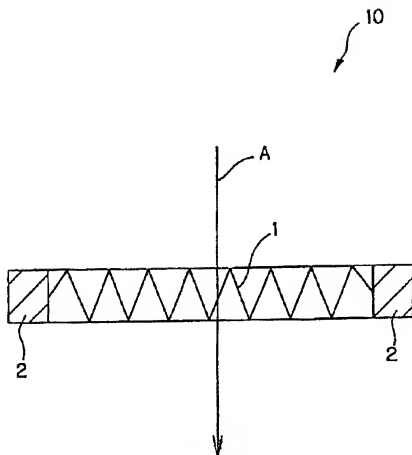


FIG. 2

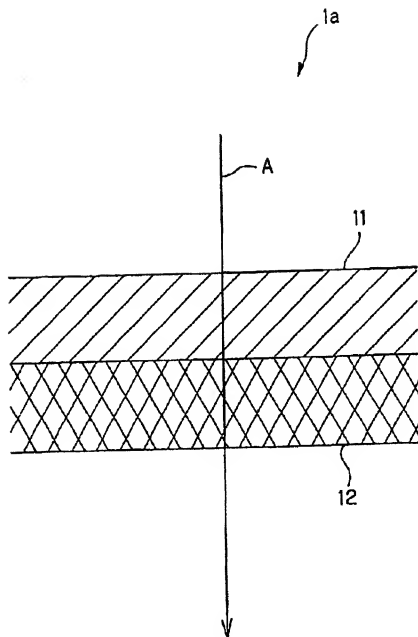


FIG. 3(A)

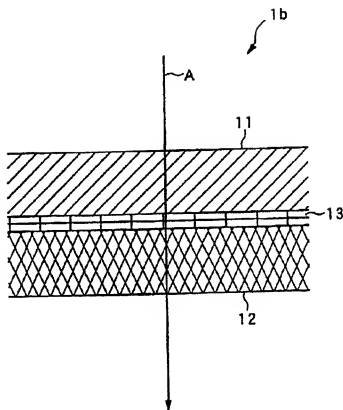


FIG. 3(B)

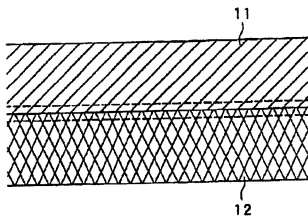


FIG. 4

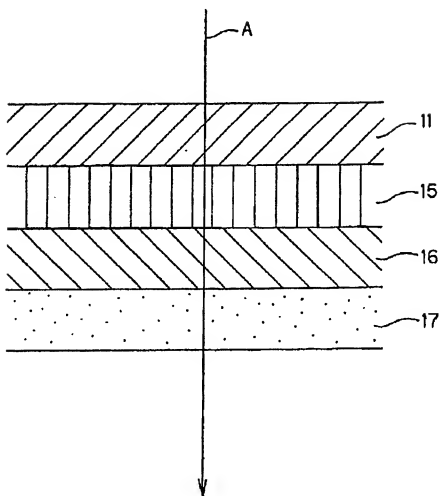


FIG. 5(A)

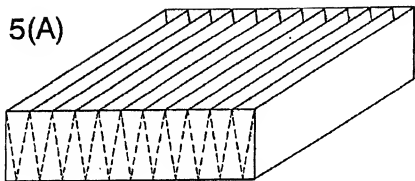


FIG. 5(B)

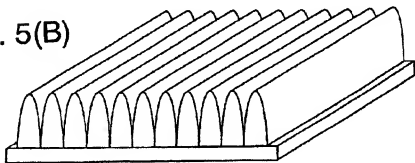


FIG. 5(C)

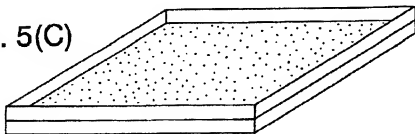


FIG. 6(A)

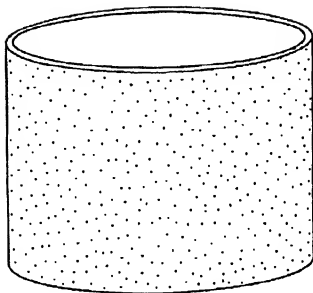


FIG. 6(B)

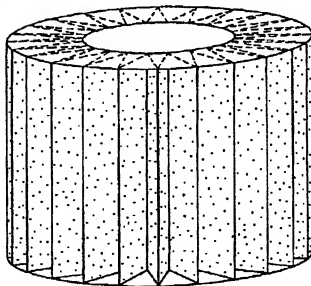


FIG. 7

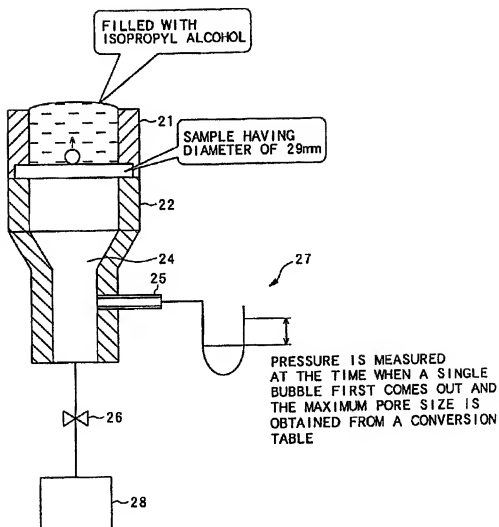


FIG. 8

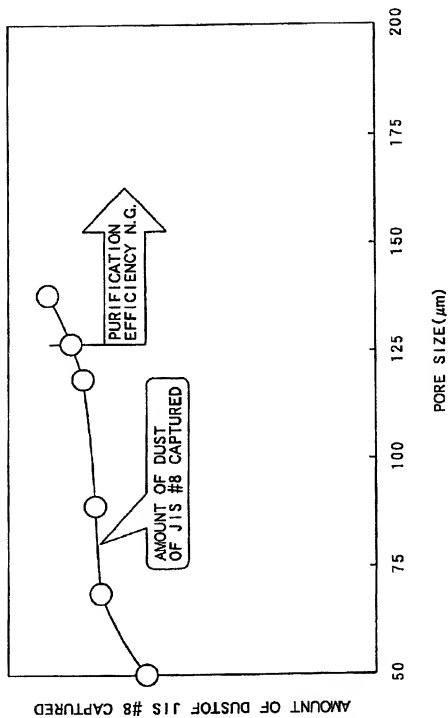
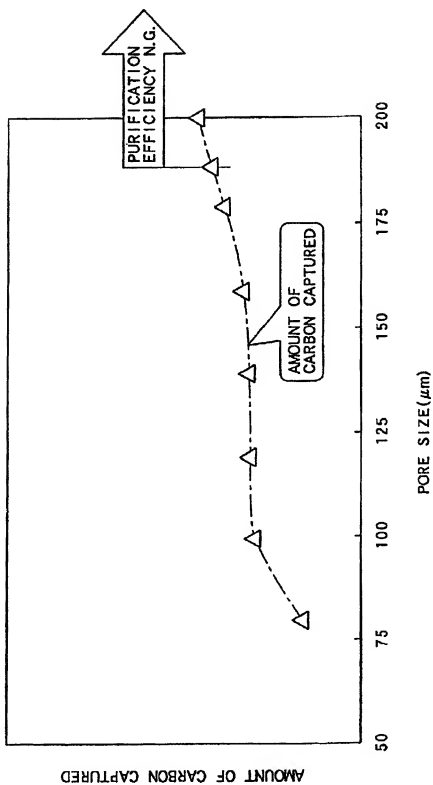


FIG. 9



AIR FILTER

TECHNICAL FIELD

The present invention relates to an air filter, and especially to an air filter, which permits to capture efficiently carbon particles.

BACKGROUND OF THE INVENTION

As an air filter for a vehicle, there has been known a wet-type filter having filter paper impregnated with oil. Viscose oil is generally used as impregnation oil. Accordingly, it is called the "viscose type" air filter. The viscose type air filter has an advantage of extended lifetime in comparison with the dry-type filter, which is not impregnated with oil. In the viscose type air filter, oil on the surface of the filter captures dust and then the oil penetrates into the captured dust so as to provide a function of capturing the other dust on the surface of the captured dust. Such a chain capture of dust permits to increase an amount of captured dust per volume of the filter.

Japanese Utility Model Publication No. S63-27767 describes the improved viscose type air filter. The air filter described in Japanese Utility Model Publication No. S63-27767 is a laminate of the first filter material having a relatively high density and the second filter material having a relatively low density. Such a laminate structure permits to make oil impregnation ratios in the first and second filter materials different from each other, resulting in prevention of clogging of the filter, providing an effective capture of dust.

The wet-type filter impregnated with oil has a problem that carbon particles cannot be captured effectively. The dry-type filter, which is not impregnated with oil, can capture effectively carbon, but has a problem of a decreased amount of captured dust per volume of the filter. Use of non-woven fabric leads may cause problems that dust permeation occurs at a high flow rate and in a serious pulsation and costs increase.

DISCLOSURE OF THE INVENTION

An object of the present invention, which was made in view of the above-described circumstances, is therefore to provide an air filter, which permits to provide a large amount of captured dust per volume of the filter, capture effectively carbon particles and reduce costs.

The present invention will be described below. Reference numerals in the accompanying drawings will be given with parentheses in order to facilitate understanding of the present invention. However, the present invention is not limited only to embodiments as illustrated.

In order to attain the aforementioned object, an air filter (10) comprises: a first filter layer (11) impregnated with oil; and a second filter layer (12) provided on a downstream side of said first filter layer, said second filter layer being composed of a lipophobic layer having an oil-repellent property, each of said first filter layer (11) and said second filter layer (12) being formed of filter paper, filter material of said first filter layer (11) having a higher density than filter material of said second filter layer (12), and said second filter layer (12) being composed of said lipophobic layer over an entire thickness.

According to the present invention, the first filter layer that is formed of the filter paper having the high density and is impregnated with oil, captures dust on the one hand, and

the second filter layer that is formed of the filter paper having the low density and subjected to an oil-repellent treatment so as not to be impregnated with oil, captures carbon particles, on the other hand, thus performing effective filtering operations by means of both filter layers. In general, the thickness of the second filter layer is determined on the basis of specification of capturing the carbon particles. According to the present invention, the second filter layer has the oil-repellent property over the entire thickness.

Consequently, the oil in the first filter layer is not carried by any portion of the second filter layer in its thickness direction, thus making it possible to cause the second filter layer over its entire thickness to capture effectively the carbon particles. On the contrary, in case where the second filter layer is provided only in the upstream portion with a lipophobic layer, the oil in the first filter layer may penetrate through the lipophobic layer, thus causing a problem that the carbon particles cannot be captured effectively over the entire thickness of the second filter layer. Each of the filter layers is formed of filter paper and it is therefore possible to prevent occurrence of dust permeation at a high flow rate and in a serious pulsation and reduce material cost to the minimum. In addition, the filter material of the first filter material has a higher density than the filter material of the second filter layer and pressure loss can also therefore be minimized.

An embodiment of the present invention is characterized in that said first filter layer and said second filter layer are combined integrally with each other.

According to the present invention, the first filter layer and the second filter layer can be combined integrally with each other, thus providing a simple layer structure. The entire thickness of the filter can be adjusted, as an occasion demands.

An embodiment of the present invention is characterized by further comprising an additional layer.

According to the present invention, the additional layer as included can improve performance of the filter element.

An embodiment of the present invention is characterized in that said first filter layer has a pore size of from 70 μm to 120 μm and said second filter layer has a pore size of from 100 μm to 180 μm .

Grounds for limiting the pore size of the first filter layer of from 70 μm to 120 μm and the pore size of the second filter layer of from 100 μm to 180 μm are described below. First, description will be given of grounds for limiting the pore size of the first filter layer of from 70 μm to 120 μm . The present inventors made an experiment on an amount of experimental dust established by the JIS (Japanese Industrial Standard) #8, which penetrates through the first filter, while gradually changing the pore size. FIG. 8 shows the results of the experiment. An abscissa denotes the pore size (μm) and an ordinate shows an amount of captured dust according to the JIS #8, which penetrates the first filter. It is recognized from FIG. 8 that, with the pore size of over 120 μm , a sieve diameter becomes large so as to increase an amount of the dust, which penetrates the first filter, deteriorating purification efficiency. On the contrary, with the pore size of less than 70 μm , an amount of the dust, which penetrates the first filter, is rapidly decreased. Consequently, an amount of the dust captured by the first filter rapidly increases, thus decreasing the lifetime of the filter.

Then, description will be given of grounds for limiting the pore size of the second filter layer of from 100 μm to 180 μm . The present inventors made an experiment on an amount of carbon, which penetrates through the second

3

filter, while gradually changing the pore size. FIG. 9 shows the results of the experiment. An abscissa denotes the pore size (μm) and an ordinate shows an amount of captured carbon, which penetrates the second filter. It is recognized from FIG. 9 that, with the pore size of over 180 μm , a sieve diameter becomes large so as to increase an amount of the carbon, which penetrates the second filter, deteriorating purification efficiency. On the contrary, with the pore size of less than 100 μm , an amount of the carbon, which penetrates the second filter, is rapidly decreased. Consequently, an amount of the dust captured by the first filter rapidly increases, thus decreasing the lifetime of the filter.

Limiting the pore sizes of the first filter layer and the second filter layer within the above-mentioned ranges makes it possible to increase the lifetime of the filter, without deteriorating purification efficiency of the filter.

An embodiment of the present invention is characterized in that said second filter layer has a downstream end, which is exposed.

According to the present invention, it is possible to prevent oil from adhering to the downstream end of the second filter, permitting a more effective capture of the carbon particles utilizing the second filter layer.

The air filter may be manufactured by subjecting the second filter layer to an oil-repellent treatment and then combining the first filter layer and the second filter layer integrally with each other, or by combining the first filter layer and the second filter layer integrally with each other, subjecting the second filter layer to the oil-repellent treatment and then impregnating the first filter layer with oil.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view illustrating an embodiment of an air filter of the present invention;

FIG. 2 is a cross-sectional view illustrating a filter element of the first embodiment;

FIG. 3 is a cross-sectional view illustrating the filter element of the second embodiment (FIG. 3(A) shows the filter element as being manufactured and FIG. 3(B) shows the filter element as completely manufactured);

FIG. 4 is a cross-sectional view illustrating the filter element of the third embodiment;

FIG. 5 is a view illustrating generally the filter element of the fourth embodiment;

FIG. 6 is a view illustrating generally the filter element of the fifth embodiment;

FIG. 7 is a view illustrating a device for measuring a pore size;

FIG. 8 is a graph illustrating the relationship between the pore size and an amount of dust captured in the first filter layer; and

FIG. 9 is a graph illustrating the relationship between the pore size and an amount of carbon captured in the second filter layer.

BEST MODE FOR CARRYING OUT THE INVENTION

Now, embodiments of an air filter of the present invention will be described below with reference to FIGS. 1 to 6.

An air filter 10 as shown in FIG. 1 is composed of a pleated filter element 1 and a frame member 2, which is formed of plastic into a rectangular shape to support the filter element 1. As shown in FIG. 1, the filter element 1 is subjected to an insert injection to form the frame member 2 to which a peripheral portion of the filter element 1 is fixed.

4

The filter element 1a of the first embodiment as shown in FIG. 2 is provided with the first filter layer 11 having filter element impregnated with oil such as viscous oil and the second filter layer 12, which is composed of a lipophobic layer having an oil-repellent property. Both the first filter layer 11 and the second filter layer 12 are formed of filter paper. The filter material of the first filter layer 11 has a higher density than the filter material of the second filter layer 12. The second filter layer 12 is formed as the lipophobic layer over the entire thickness, i.e., from the upstream-side end face 12a to the downstream-side end face 12b so as to prevent or inhibit oil impregnated in the first filter layer 11 from entering the oil-repellent property of the lipophobic layer. The downstream-side end face 12b of the second filter layer 12 is exposed to come into contact with air. The upper surface of the first filter layer 11 oozes with the oil impregnated in the first filter layer 11 to provide a condition in which dust can easily be captured. Imparting the oil-repellent property to the second filter layer 12 makes it possible to provide a filter layer for capturing carbon particles, which have not been captured by the first filter layer 11 impregnated with the oil and passed through the first filter layer 11, under the function of contact filtration.

The lipophobic property can be imparted to the second filter layer 12 with the use of material as properly selected, having the oil-repellent property such as filter paper impregnated with fluorine contained resin. The first filter layer to be impregnated with oil by the subsequent step and the second filter layer, which is formed of filter paper to be impregnated with the above-mentioned fluorine contained resin may be combined together in the paper manufacturing process. It is also possible to provide a combined body of the above-mentioned two layers utilizing a method comprising the steps of combining the first filter layer and the second filter layer together (for example into a filter layer having a single layer structure), impregnating the first filter layer (for example the upper half portion of the above-mentioned single filter layer) with oil and applying lipophobic agent to the second filter layer (for example the lower half portion of the above-mentioned single filter layer). In such a case, an application method such as a spraying method, a roller coating method (such as a direct roller coating method and a kiss-roll coating method), a dipping method and the other method is applicable. Such an application method provides advantages of forming the lipophobic layer with an easy process.

In the second embodiment as shown in FIG. 3(A), the filter element 1b is obtained by combining the first filter layer 11 having the filter material impregnated with oil and the second filter layer 12 composed of the lipophobic layer by an adhesive layer 13. The first filter layer 11 and the second filter layer 12 are joined together so as to permit air to pass through the contacting surfaces of these layers. After completion of the manufacturing steps, the adhesive agent 13 permeates into the first filter layer 11 and the second filter layer 12 so as not to form any gap between the first filter layer 11 and the second filter layer 12 as shown in FIG. 3(B). Also in the embodiment the upper surface of the first filter layer 11 oozes with the oil impregnated in the first filter layer 11 to provide a condition in which dust can easily be captured. Imparting the oil-repellent property to the second filter layer 12 makes it possible to provide a filter layer for capturing carbon particles under the function of contact filtration. The embodiment describes the state in which no gap is formed between the first filter layer 11 and the second filter layer 12 after completion of the manufacturing steps.

5

The adhesive layer 13 may however be left between the first filter layer 11 and the second filter layer 12 so that these layers 11 and 12 are apart from each other.

In the method for manufacturing the filter element of the embodiment, the first filter element 11 and the second filter element 12 are placed one upon another through the adhesive agent to combine them together and then the first filter layer 11 is impregnated with oil.

As the adhesive agent used for the adhesive layer 13, it is preferable to select and use for example a hot-melt material, taking into consideration the manufacturing steps of the filter and conditions under which the filter is manufactured is used. Such a hot-melt material may include olefin material or polyester material.

In the first and second embodiments, an appropriate value may be selected, as the pore size of the first filter layer 11, for example from the range of 70 μm to 120 μm in accordance with a performance required for the air filter. The capturing efficiency of dust in the first filter layer 11 is determined so that the filter sieve can capture the dust. Consequently, the value of the pore size is set taking into consideration the particle size of the dust to be captured and pressure loss.

The pore size of the second filter layer 12 having the lipophobic property is set for example to a value within the range of from 100 μm to 180 μm . Such a setting leads to the pore size of the entire filter element of 70 μm to 120 μm . A reason for using the filter material having a relatively large pore size for the second filter layer 12 is that the second filter layer 12 is to be used to capture carbon particles under the function of contact filtration and it is unnecessary to make the filter material dense. Making the filter material of the second filter layer 12 sparser than the filter material of the first filter layer 11 can rather reduce pressure loss.

The filter element 1 of the third embodiment as shown in FIG. 4 is provided with the first filter layer 11 having the filter material impregnated with oil, the first intermediate layer 15, the second intermediate layer 16 and a clean layer 17, which are disposed in this order from the upstream side to the downstream side. In the embodiment, the second filter layer composed of the lipophobic layer having the oil-repellent property serves as any one of the first intermediate layer 15, the second intermediate layer 16 and the clean layer 17. With respect to the other layer, material, a pore size, thickness and the other conditions may be determined taking into consideration object of use of the filter. The material for the other layer may be formed for example of filter paper or non-woven fabric. In case where the filter paper is used, a water-repellent treatment applied to it makes it possible to prevent water from being sucked into the inside of an engine, even when a suction port of an intake system is located in a place in which water is easily be sucked.

Now, a filtering operation of the air filter of the embodiment of the present invention will be described. An arrow with a reference symbol "A" in FIGS. 1 to 4 denotes a flowing direction of air. As shown in FIGS. 2 to 4, air first passes through the first filter layer 11 and then through the second filter layer.

As described above, the first filter layer 11 is a wet-type filter layer, which is impregnated with oil. A dense structure of the filter material and existence of oil impregnated therein are essential to effective capture of dust. A condition that the filter layer, which is dense and impregnated with oil, exists so as to face an air passage, is also essential to a sufficient capture of dust. Accordingly, use of the first filter layer 11, which satisfies these conditions, makes it possible to effectively capture dust in the air. However, the filter material impregnated with oil cannot generally provide an effective capturing effect of carbon particles in the air. More

6

specifically, what can effectively be captured by means of the first filter layer 11, is dust other than the carbon particles.

The air, which has passed through the first filter layer 11, enters the second filter layer 12. The second filter layer 12, which is the lipophobic filter having the oil-repellent property and has the sparse (i.e., low density) filter material, can provide an effective capture of the carbon particles. The second filter layer 12 may capture the carbon particles under the function of contact filtration.

According to the air filter of each embodiment of the present invention, the first filter layer 11 effectively captures dust other than carbon particles and the second filter layer 12 effectively captures, over its entirety in the thickness direction, the carbon particles, which have passed through the first filter layer 11. Consequently, the air filter as a whole effectively captures both of the carbon particles and the other dust. In the embodiment of the present invention, the second filter layer 12 captures the carbon particles under the function of contact filtration, unlike the conventional air filter in which the filter materials are disposed so that the density of the filter materials becomes higher in the downstream direction of the flow of air. As a result, it is possible to make the density of the filter material of the second filter layer 12 lower than that of the first filter layer 11, thus reducing pressure loss.

In the wet-type filter, oil generally moves to the downstream side of flow of air through a phenomenon called "carrying off" by air. In the air filter of the embodiment of the present invention, the second filter layer 12 serving as the lipophobic layer is provided on the downstream side of the first filter layer 11. There is ensured a state in which oil does not easily moves to the second filter layer 12 under the function of the oil-repellent property of the lipophobic layer.

In general, an amount of oil impregnated in the filter layer has an influence on the property of capturing carbon particles so that impregnation of the filter layer with oil lower the capturing property. Accordingly, if the second filter layer 12 is impregnated with oil, the carbon particles cannot be captured effectively. In the embodiment of the present invention, the second filter layer 12 is the lipophobic layer as described above so as to prevent the oil from moving. As a result, almost no movement of oil from the first filter layer 11 to the second filter layer 12 occurs. The second filter layer can be kept free from oil, thus making it possible to maintain a high capturing property by which carbon particles can be captured effectively for a long period of time.

In addition, oil does not easily move to the second filter layer 12 and there is no possibility that the oil is carried to the further downstream side of the second filter layer 12. Accordingly, when the air filter of the embodiment of the present invention is mounted on an intake system of an engine for a vehicle, there occurs no inconvenience that the oil is sucked into the downstream side of the air filter. In case where the third filter layer and the fourth filter layer are provided on the downstream side of the second filter layer 12, it is therefore preferable to arrange them so that the densities of these filter layers becomes lower in the flowing direction of air.

In case where the air filters in both embodiments of the present invention are used as an air filter for a vehicle, it is preferable to limit the entire thickness of the filter element 1 within the range of from 0.80 mm to 3.50 mm, and more preferably within the range of from 0.90 mm to 1.75 mm. In such a case, it is preferable to limit the thickness of the first and second filter layer within the range of from 0.3 mm to 0.75 mm and the second filter layer within the range of from 0.6 mm to 1.00 mm.

In the embodiment of the present invention, the filter element 1 is pleated so as to increase the substantial area of

the filter, as shown in FIGS. 1 to 6. The filter element 1 may be used in an extended flat state as shown in FIG. 5(c). FIGS. 5(a) and 5(b) illustrate examples of the filter elements 1, which are pleated into a panel-shaped filter. It is also possible to form the filter elements 1 into a tubular shape and a chrysanthemum shape as shown in FIGS. 6(a) and (b), respectively, so that air can pass through the filter elements 1 from the inside to the outside, and vice versa. The shape of the filter element can be selected freely in such a manner.

when a single bubble first comes from the upper surface of the filter 23 into the isopropyl alcohol.

A pore size (μm) is obtained on the basis of the thus obtained pressure difference utilizing a conversion table indicated below. The conversion table as conventionally used utilizes a unit "mmHg" for the pressure. A unit "Pa" according to the SI unit system is also indicated in the following table.

TABLE 1

PRESSURE mmHg	PRESSURE Pa	PORE SIZE μm	PRESSURE mmHg	PRESSURE Pa	PORE SIZE μm	PRESSURE mmHg	PRESSURE Pa	PORE SIZE μm
50	490.0	254.3	84	823.2	128.6	118	1156.4	86.0
51	499.8	247.2	85	833.0	126.7	119	1166.2	85.2
52	509.6	240.5	86	842.8	124.9	120	1176.0	84.4
53	519.4	234.1	87	852.6	123.2	121	1185.8	83.6
54	529.2	228.1	88	862.4	121.5	122	1195.6	82.8
55	539.0	222.3	89	872.2	119.8	123	1205.4	82.0
56	548.8	216.9	90	882.0	118.2	124	1215.2	81.3
57	558.6	211.7	91	891.8	116.7	125	1225.0	80.5
58	568.4	206.7	92	901.6	115.2	126	1234.8	79.8
59	578.2	202.0	93	911.4	113.7	127	1244.6	79.1
60	588.0	197.5	94	921.2	112.2	128	1254.4	78.4
61	597.8	193.2	95	931.0	110.8	129	1264.2	77.7
62	607.6	189.0	96	940.8	109.5	130	1274.0	77.0
63	617.4	185.1	97	950.6	108.1	131	1283.8	76.4
64	627.2	181.3	98	960.4	106.8	132	1293.6	75.7
65	637.0	177.6	99	970.2	105.5	133	1303.4	75.1
66	646.8	174.1	100	980.0	104.3	134	1313.2	74.4
67	656.6	170.8	101	989.8	103.1	135	1323.0	73.8
68	666.4	167.5	102	999.6	101.9	136	1332.8	73.2
69	676.2	164.4	103	1009.4	100.7	137	1342.6	72.6
70	686.0	161.4	104	1019.2	99.0	138	1352.4	72.0
71	695.8	158.5	105	1029.0	98.5	139	1362.2	71.4
72	705.6	155.7	106	1038.8	97.4	140	1372.0	70.8
73	715.4	153.0	107	1048.6	96.3	141	1381.8	70.3
74	725.2	150.4	108	1058.4	95.3	142	1391.6	69.7
75	735.0	147.9	109	1068.2	94.3	143	1401.4	69.2
76	744.8	145.5	110	1078.0	93.3	144	1411.2	68.5
77	754.6	143.1	111	1087.8	92.3	145	1421.0	68.1
78	764.4	140.8	112	1097.6	91.4	146	1430.8	67.6
79	774.2	138.6	113	1107.4	90.4	147	1440.6	67.1
80	784.0	136.5	114	1117.2	89.5	148	1450.4	66.6
81	793.8	134.4	115	1127.0	88.6	149	1460.2	66.1
82	803.6	132.4	116	1136.8	87.7	150	1470.0	65.6
83	813.4	130.4	117	1146.6	86.9	151	1479.8	65.1

Brief description will be given below of a testing method for measuring the pore size set forth in the above-described embodiments, with reference to FIG. 7. A disk-shaped filter 23, which serves as a sample and having a diameter of 29 mm, is held air-tightly between two aluminum pipes 21, 22. The lower aluminum pipe 22, which is placed below the filter 23, is provided on the lower end side with a valve 26 for maintaining a constant pressure of air in the pipe 22. The valve 26 is connected to an air supply device 28 having an air compressor.

An air sampler pipe 25 is fitted to the side surface of the aluminum pipe 22. The air sampler pipe 25 is connected to a pressure gauge 27. The pressure gauge 27 can measure the pressure of the inside 24 of the aluminum pipe 22 in this manner.

Prior to measurement of the pore size, the aluminum pipe 21, which is placed above the filter 23, is filled with isopropyl alcohol. The inside 24 of the aluminum pipe 22 is equal to the atmospheric pressure. Then, the valve 26 is gradually opened to supply air from the air supply device 28 so as to gradually increase the pressure of the inside 24 of the aluminum pipe 22. Pressure difference between the atmospheric pressure and the inside 24 of the aluminum pipe 22 is measured utilizing the pressure gauge 27 at the time

According to the present invention, the first filter layer, which is formed of a dense filter paper and impregnated with oil, captures dust and the second filter layer, which is formed of a sparse filter paper and is not impregnated with oil, captures carbon particles so that the both filter layers can perform an effective filtration. In addition, the second filter layer has the lipophobic property over its entire thickness. The oil of the first filter layer is not carried to any portion of the second filter layer, thus making it possible for the second filter layer to capture effectively the carbon particles over its entire thickness. Further, the filter material of the second filter layer is sparser than the filter material of first filter layer, thus reducing pressure loss.

What is claimed is:

1. An air filter comprising:

- a first filter layer formed of a first filter paper material having a predetermined density, said first filter layer being impregnated with oil; and
- a second filter layer provided on a downstream side of said first filter layer so as to be independent from said first filter layer, said second filter layer being formed of a second filter paper material having a lower density than said predetermined density of said first filter layer,

9

said second filter layer being impregnated over its entirety with an oil-repellent agent.

2. The air filter as claimed in claim 1, wherein:

said first filter layer and said second filter layer are combined integrally with each other.

3. The air filter as claimed in claim 1, further comprising an additional layer.

4. The air filter as claimed in claim 1, wherein:

said first filter layer has a pore size of from 70 μm to 120 μm and said second filter layer has a pore size of from 100 μm to 180 μm .

5. The air filter as claimed in claim 1, wherein:

said second filter layer has a downstream end, which is exposed.

6. The air filter as claimed in claim 2, wherein:

said second filter layer is subjected to an oil-repellent treatment and then said first filter layer and said second filter layer are combined integrally with each other.

7. The air filter as claimed in claim 2, wherein:

said first filter layer and second filter layer are combined integrally with each other; and then,

said second filter layer is subjected to an oil-repellent treatment and said first filter layer is impregnated with oil.

8. The air filter as claimed in claim 2, further comprising an additional layer.

9. The air filter as claimed in claim 3, wherein:

said first filter layer has a pore size of from 70 μm to 120 μm and said second filter layer has a pore size of from 100 μm to 180 μm .

10. The air filter as claimed in claim 3, wherein:

said second filter layer is subjected to an oil-repellent treatment and then said first filter layer and said second filter layer are combined integrally with each other.

11. The air filter as claimed in claim 3, wherein:

said first filter layer and second filter layer are combined integrally with each other; and then,

said second filter layer is subjected to an oil-repellent treatment and said first filter layer is impregnated with oil.

12. A air filter, comprising:

a first layer of a first filter paper impregnated with oil; and a second layer of a second filter paper placed in a downstream air direction adjacent the first layer,

10

a density of the first filter paper being greater than a density of the second filter paper, the second layer formed as an oil-repellent lipophobic layer over an entire thickness of the second layer.

13. The filter of claim 12, wherein,

a downstream face of the second layer is exposed to air, an upper, upstream face of the first layer oozes with the oil.

14. The filter of claim 12, wherein the second layer is impregnated with a resin containing fluorine.

15. The filter of claim 12, further comprising:

an adhesive layer binding the first layer with the second layer with the first and second layers contacting one another,

the adhesive layer penetrating a downstream side of the first layer and an upstream side of the second layer.

16. The filter of claim 15, wherein the adhesive layer comprises one of an olefin material and a polyester material.

17. The filter of claim 12, wherein,

the first layer has a pore size of from 70 μm to 120 μm and the second filter layer has a pore size of from 100 μm to 180 μm .

18. A air filter, comprising:

a first layer of a first filter paper impregnated with oil; a second layer of a second filter paper placed in a downstream air direction contacting the first layer; and a hot-melt adhesive layer binding the first layer with the second layer, the adhesive layer penetrating a downstream side of the first layer and an upstream side of the second layer,

a density of the first filter paper being greater than a density of the second filter paper, the second layer formed as an oil-repellent lipophobic layer over an entire thickness of the second layer.

19. The filter of claim 18, wherein the second layer is impregnated with a resin containing fluorine.

20. The filter of claim 18, wherein,

the first layer has a pore size of from 70 μm to 120 μm and the second filter layer has a pore size of from 100 μm to 180 μm .

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